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(54) Title: **A COMPOSITION COMPRISING A METAL SALT AND METAL POWDER THEREFROM BY THE CALCINING THEREOF**

(57) Abstract

Disclosed is a composition of an essentially solid phase state having as components, a liquid hydrophilic organic polymer, an aqueous salt solution containing at least one metallic or metalloid element, and a coagulating agent. The composition on calcination provides a metal-containing powder having an average particle size of 1 micrometer or less. Such metal-containing powders are of value in the preparation of industrial catalysts, ceramics, electronic components, or as fillers in plastics, paints or cosmetics.

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A COMPOSITION COMPRISING A METAL SALT AND METAL POWDER THEREFROM BY
THE CALCINING THEREOF

This invention relates to a composition which comprises a liquid hydrophilic polymer, an aqueous salt solution of a metallic or metalloid element, and a coagulating agent; and a process for preparing a metal-based powder by calcining the said composition.

Metal or metal oxide particles of submicron size are a valuable industrial commodity finding use in many applications including, for example, in the manufacture of industrial catalyst such as might be employed in the chemical industry, in the manufacture of ceramics, of electronic components, and as fillers for, for example, plastics, paints or cosmetics.

A large variety of techniques are available for the manufacture of metal or metal oxide powders having a very fine particle size. Such techniques include solution processes and high temperature gas phase and condensed phase syntheses. For a comprehensive review of the general techniques available, reference is made to the recent publication entitled "Chemical Engineering Aspects of Advanced Ceramic Materials" by V. Hlavacek and J.A. Puszynski published in the Journal of Industrial Engineering and Chemical Research, pages 349-377, Volume 35, 1996.

Despite the numerous procedures available, a problem in common to a lesser or greater extent with nearly all methods is the difficulty of obtaining consistently fine uniform particles of good purity. Procedures that can provide a greater consistency in this respect invariably have high costs associated with their operation due to the complexity of the equipment required, the use of expensive and potentially hazardous raw materials, or high energy consumption. Recently two closely related procedures have been published which provide a means of manufacturing submicron sized metal powders without need of complex and costly equipment. In the publication EP-A-621,234 to manufacture metal powders it is required to calcine a polyurethane polymer containing a metal salt; however yields are relatively low. In another publication, WO96/29280 this polyurethane approach has been modified by avoidance of the use of polyisocyanate, a hazardous chemical, with the requirement to subject to calcination a gel or liquid. Gels are difficult to handle or manipulate in such a calcining procedure; handling of solids is highly preferred.

It would therefore be desirable to develop a cost effective procedure leading to the production of metal or metal oxide powders having a consistently fine particle size. It would be of particular advantage if such a procedure could be operated using raw materials readily available and could be operated in the substantial absence of highly specialized

equipment and costly solvents or chemical processing aids. It would also be an advantage if such a procedure were able to provide for the production of metal powders in a more attractive yield by calcination of solids in contrast to gels which are notoriously difficult to handle in industrial procedures.

5 In a first aspect, this invention relates to a composition with as components:

- a) a liquid hydrophilic organic polymer; and
- b) an aqueous salt solution containing at least one metallic or metalloid element;

10 characterized in that the composition further comprises (c) a coagulating agent, and wherein the salt is present in an amount to provide the composition with metallic or metalloid element content of at least 1 weight percent based on total weight of the composition.

15 In a second aspect, this invention relates to a process for preparing a metal-based powder, having a mean particle size of less than 1 micrometer, by calcining at a temperature of from 300°C to 3000°C, a composition that comprises:

- a) liquid hydrophilic organic polymer; and
- b) an aqueous salt solution containing at least one metallic or metalloid element;

20 characterized in that the composition further comprises (c) a coagulating agent, and the salt is present in an amount to provide the composition with metallic or metalloid element content of at least 1 weight percent based on total weight of the composition.

25 In a third aspect, this invention relates to a method for solidifying a mixture which contains a liquid hydrophilic organic polymer with an aqueous salt solution of at least one metallic or metalloid element which comprises adding to said mixture a coagulating agent or precursor thereto.

30 During the present investigations it has been discovered that when a coagulating agent is added to a mixture of a hydrophilic organic polymer, notably a polyether polyol, with an aqueous metal salt solution that the resulting composition takes on a substantially solid, or semi-solid state. It has further been discovered that when such a solid substance is calcined a metal powder of submicron particle size is obtained wherein the BET surface area

of the resulting powder can be enhanced through the use of a polyether polyol selected in consideration of having an elevated oxyethylene content.

The present invention provides for a relatively simple and cost-effective route for the manufacture of metal-containing powders of submicron particle size. Such particles find 5 value in the manufacture of ceramic articles, electronics, industrial catalysts and as fillers in plastics, paints or cosmetics including creams and oils. When used as filler, the smaller particle of the filler provide for a minimum reflection of visible light allowing exploitation of 10 filler properties with minimal disturbance to transparency or visible light transmission properties of the substance to be filled. Transmission of electromagnetic radiation of other wavelengths may be blocked by the presence of the filler.

Disclosed herein is a composition that is a non-fluid substance of an essentially solid, or semi-solid, phase. The composition comprises as first component, a hydrophilic polymer formerly having a liquid phase; as second component, an aqueous salt solution of a metallic or metalloid substance; and is characterized in that it contains as third component, a 15 coagulating agent.

The metallic or metalloid element content of the composition, excluding the counter ion and any water of crystallization, is at least 1 weight percent based on total weight of the composition. Advantageously the metallic or metalloid element content is at least 3 weight percent, preferably at least 5 weight percent, and yet more preferably at least 10 20 weight percent. While a lesser amount can in principle be present, this is against the interest of obtaining a high yield of metal powder in the subsequent calcining process. In practice, the upper amount of metal salt present will be limited by its solubility limit in water and concomitantly the miscibility with the hydrophilic polymer.

The individual components of the composition are described in more detail 25 hereinafter.

The hydrophilic polymer component of the composition initially has a liquid phase and can be any inorganic or organic polymer exhibiting a hydrophilic trait including, as examples, polyethers, polyamides and polyesters. Organic polymers are preferred due to their ability to be calcined or pyrolyzed without any notable accumulation of a solid residue. 30 Suitable hydrophilic organic polymers include polyether polyols, preferably poly(oxyalkylene-oxyethylene) polyols, and more preferably poly(oxyalkylene-oxyethylene) polyols where the oxyethylene content is randomly distributed throughout the molecule. The oxyalkylene

portion of the polyol can be oxyethylene, however, oxypropylene or oxybutylene is preferred. When a poly(oxyalkylene-oxyethylene) polyol, is selected as the hydrophilic organic polymer component, advantageously the oxyethylene content of the polyol is from at least 35, and preferably from at least 50, weight percent of the total molecular weight of the polyol. During 5 our investigation, little or no influence of polyol molecular weight on the properties of the resulting metal-based powder has been observed. However, for convenience of preparing the composition, it is advantageous to select a polyether polyol having a molecular weight in the range of 500 to 10000, preferably from 1000 to 6000. Exemplary of suitable polyether polyols include glycerine-initiated oxypropylene polyols such as VORANOL™ 1055 10 (molecular weight 1000); and glycerine-initiated oxypropylene-oxyethylene polyols such as VORANOL 1421 (molecular weight 5000, 75 weight percent ethylene oxide of random distribution), both being available from The Dow Chemical Company.

The second component of the composition is an aqueous salt solution which comprises one or more metallic or metalloid elements. Advantageously such metallic or 15 metalloid elements are those as defined in the Periodic Table of Elements selected from Groups 2a, 3a, 4a, 5a, 6a; 2b, 3b, 4b, 5b, 6b, 7b, 8, 1b and 2b; the lanthanide elements; and the actinide elements. The metallic or metalloid element can in principle be of any element from which it is desired to obtain a powder. However those presently having known 20 industrial value and suitable for use in the present invention include lanthanum, barium, strontium, chromium, zirconium, yttrium, aluminum, lithium, iron, antimony, bismuth, lead, calcium, magnesium, copper, boron, cadmium, cesium, cerium dysprosium, erbium, europium, gold, hafnium, holmium, lutetium, mercury, molybdenum, niobium, osmium, palladium, platinum, praseodymium, rhenium, rhodium, rubidium, ruthenium, samarium, scandium, sodium, tantalum, thorium, thulium, tin, zinc, nickel, titanium, tungsten, uranium, 25 vanadium, or ytterbium, or a mixture of two or more thereof.

The concentration of salt present in the water is as high as practically possible in consideration of its solubility limit. Where possible it is preferred to use aqueous compositions which are essentially saturated solutions at ambient temperature.

In this invention by the term "coagulating agent" it is generally meant any 30 substance which is able to induce coagulation, that is, to induce a change from a fluid state to a solid or semi-solid state.

The coagulating agent can be an organic or inorganic substance having an aqueous pH value of less than 7 (acidic), or greater than 7 (basic). Advantageously the substance should not leave any residue after pyrolysis/calcining. When the coagulating agent is an organic substance, suitable are primary- or secondary-, amines, amides or 5 alkanolamines. Particularly suitable are, for example, monoethanolamine or diethanolamine. When the coagulating agent is an inorganic substance, suitable basic substances include, for example, ammonium hydroxide, ammonium hydrogen carbonate, ammonium carbonate. Exemplary of inorganic, acidic coagulating agents include hydrogen sulfide.

Especially preferred as coagulating agent in this invention is ammonium 10 hydroxide due to its high basicity and attractive water solubility leading to a rapid coagulation result. Ammonium hydroxide may be introduced as an aqueous solution or alternatively generated *in situ* by use of a precursor. Examples of precursors include ammonia gas and urea. Urea on exposure to thermal energy undergoes decomposition leading to generation of nascent ammonia which in the aqueous environment provides for immediate formation of 15 ammonium hydroxide. Formation of ammonium hydroxide by way of urea provides for an extremely effective distribution of the coagulating agent throughout the composition which in many instances is superior to that which can be achieved by direct introduction and mechanical mixing.

It is presently believed that a high coagulation rate is required so that a fine 20 dispersion of the salt in the polymer is obtained. In contrast it is believed that a lower coagulation rate provides an undesirable opportunity for growth of metal salt crystals during the coagulation event. Such crystal formation provides a locally high concentration of metal salt within the polymer which subsequently on calcining may lead to the formation of particles having a larger particle size.

25 The composition of this invention can be prepared by a variety of addition sequences which include simultaneously mixing all components, or alternatively blending any two components and subsequently introducing the final component. To facilitate the eventual formation of metal powders having a small average particle size/large surface area, it is found advantageous to first mix the hydrophilic organic polymer with the aqueous metal 30 solution and subsequently introduce the coagulating agent. When employing urea as a coagulant precursor, after the initial mixing it is necessary to induce decomposition of the urea by subsequent exposure to, for example, thermal energy. Alternative energy sources can also be used for the same purpose.

Any equipment commonly used in blending viscous liquids can be employed to produce the composition of this invention. Such equipment provides for the efficient mixing, under high shear conditions, of controlled amounts of aqueous base solution with the aqueous composition comprising both the metal salt and the polymeric composition.

5 The disclosed composition when calcined under controlled conditions, providing for the removal of the all organic substance, results in the formation of a substantially uniformly sized, agglomerate-free, metal-containing powder. Typically the calcining conditions require exposing the composition to a temperature of from 300°C to 3000°C, and preferably from 400°C to 1000°C for a period of a few minutes to many hours. To assist in 10 removal of the organic polymer, prior to calcining, optionally a pyrolysis step may be employed. The term "metal-containing" can mean that the powder contains metal as an element, or an oxide, or other adduct including for example, a carbide or an alloy thereof, a sulfide or a nitride. Whether a powder which is obtained will be a metal, a metal alloy, an 15 oxide or a carbide will depend upon the metal salt(s) present in the composition and the conditions of pyrolysis or calcining. It is also to be appreciated that the same factors can influence the characteristics of the particles including their size and surface area.

The metal-containing powder obtained according to this invention is characterized in that it has an average particle size of less than 1 micrometer (1000 nanometers), preferably less than 0.1 micrometer (100 nanometers), and more preferably less than 0.02 micrometer (20 nanometers). With reference to the particle size it is to be appreciated that there will be a particle size distribution where less than 50, preferably less than 25, and more preferably less than 10 percent of the particles will have a particle size in 20 excess of the previously mentioned average particle size. By the term "particle size" it is meant the size of the particle in its largest dimension. The powder is further characterized in that it has a BET surface area of at least 5, preferably at least 25, more preferably at least 25 25 50 m²/gram. In a preferred embodiment the metal-containing powder has an average particle size of less than 0.1 micrometer and a BET surface area of at least 25 m²/gram.

The powder obtainable according to this invention can comprise any desired metal. Advantageously the metal, in a zero or appropriate oxidation state, is one or more of 30 the elements lanthanum, barium, strontium, chromium, zirconium, yttrium, aluminum, lithium, iron, antimony, bismuth, lead, calcium, magnesium, copper, boron, cadmium, cesium, dysprosium, erbium, europlum, gold, hafnium, holmium, lutetium, mercury, molybdenum, niobium, osmium, palladium, platinum, praseodymium, rhenium, rhodium, rubidium, ruthenium, samarium, scandium, sodium, tantalum, thorium, thulium, tin, zinc, nickel, 35 titanium, tungsten, uranium, vanadium, or ytterbium.

5 The described metal-containing powders having a submicron particle size are of value in the manufacture of ceramic articles, industrial catalysts, electronic components, and as fillers for plastics, paints or cosmetics. When used as filler the metal-containing powder will be present, based on total weight of bulk matrix and powder, typically in an amount of from 0.1 to 50, and more usually in an amount of from 1 to 25 weight percent. The bulk matrix, may be, for example, a plastic including a thermoset or thermoplastic polymer, a paint, or a cosmetic composition cream or oil.

10 The invention is illustrated by way of the following Examples. Unless otherwise indicated all amounts are expressed as parts by weight (pbw).

Example 1

A number of compositions were prepared by blending of components in the sequence as given in accompanying Table 1. The sequence was indicated by {number} where {1} was first, {2} second and so forth.

15 The salt solution was prepared by dissolving 50 gr ZrO(NO₃)₂•xH₂O/Ce(NO₃)₃•6H₂O in a parts by ratio of 6.14:1 in 40 gr H₂O.

20 Amounts in pbw of the various components blended in the indicated order and fashion were as follows:

POLYOL	30 pbw
SALT	38.9 pbw
SALT SOLUT	70 pbw
BASE	20 or 60 pbw

25 Subsequent pyrolysis/calcining of the resulting compositions at 700°C resulted in metal powders with a BET surface area, as described by S. Brunauer, P.H. Emmett and E. Teller, J. Am. Chem. Soc. 60 (1938) 309. All BET measurements were carried out using a PULSE CHEMISORB 2700 from Micromeritics Instrument Corporation. Particle sizes were calculated from measured BET surface areas in combination with CeO₂ and ZrO₂ densities as reported in the Handbook of Chemistry and Physics, 76th edn, CRC Press, 1995.

Metal Salt: $\text{ZrO}(\text{NO}_3)_2 \bullet x\text{H}_2\text{O}/\text{Ce}(\text{NO}_3)_6 \bullet 6\text{H}_2\text{O}$ in a parts by ratio of 6.14:1.

CP1421 a glycerine-initiated oxypropylene-oxyethylene polyol of 5000 molecular weight having a randomly distributed oxyethylene content of 70 weight percent.

5 CP1055 a glycerine-initiated oxypropylene polyol of 1000 molecular weight.

Base Ammonium Hydroxide, 25 percent aqueous solution

Salt Solution metal salt as above in water to maximum solubility.

10 Examples 1 to 14 and 33 were comparative examples, Examples 15 to 32 were supportive to the disclosed invention. The data in Table 1 demonstrate the following:

- 15 a) Use of an aqueous metal salt solution in preference to a dry salt provides for a metal powder with a greater surface area;
- b) A three-component system generally provides for metal powder having a greater surface area than a two-component system;
- 20 c) Use of a polyoxyalkylene-oxyethylene polyol was preferred to use of a polyoxyalkylene polyol when desiring to obtain metal powder with a greater surface area;
- d) Examples 21 to 26 were suggestive that the order of addition of sequence does not significantly influence the surface area property of the resulting metal powder.

Table 1

Ex- ample	Hydrophilic Organic Polymer { } Sequence in blending	Metal Salt { } Sequence in blending	Base { } Sequence (pbw)	BET Surface Area m ² /g	Particle size (nm)		
	CP1055	CP1421	Dry	Aqueous			
1	/	/	/	{1}	/	10	102
2	/	/	{1}	/	{2}(20)	5	204
3	/	/	/	{1}	{2}(60)	4	255
4	{2}	/	{1}	/	/	11	93
5	/	{2}	{1}	/	/	12	85
6	/	/	/	{2}	{1}(20)	2	509
7	{2}	/	/	{1}	/	20	51
8	/	{2}	/	{1}	/	31	33
9	{3}	/	{1}	/	{2}(20)	10	102
10	/	{3}	{1}	/	{2}(20)	12	85
11	{1}	/	/	{2}	/	19	54
12	/	{1}	/	{2}	/	28	36
13	{2}	/	{1}	/	{3}(20)	9	113
14	/	{2}	{1}	/	{3}(20)	11	93
15	{3}	/	/	{1}	{2}(20)	42	24
16	/	{3}	/	{1}	{2}(20)	50	20
17	{3}	/	/	{1}	{2}(60)	29	35
18	/	{3}	/	{1}	{2}(60)	50	20
19	{3}	/	/	{2}	{1}(20)	38	27
20	/	{3}	/	{2}	{1}(20)	41	25
21	{2}	/	/	{1}	{3}(20)	34	30
22	/	{2}	/	{1}	{3}(20)	61	17
23	{2}	/	/	{3}	{1}(20)	35	29
24	/	{2}	/	{3}	{1}(20)	54	19
25	{1}	/	/	{2}	{3}(20)	36	28
26	/	{1}	/	{2}	{3}(20)	60	17
27	{1}	/	/	{2}	{3}(60)	40	25
28	/	{1}	/	{2}	{3}(60)	60	17
29	{1}	/	/	{3}	{2}(20)	40	25
30	/	{1}	/	{3}	{2}(20)	53	19
31	{1}	/	/	{3}	{2}(60)	46	22
32	/	{1}	/	{3}	{2}(60)	49	21
33	/	/	/	{1}	{2}(60)	6	170

1. A composition with as components:

- a) a liquid hydrophilic polymer; and
- b) an aqueous salt solution containing at least one metallic or metalloid element;

5 characterized in that the composition further comprises (c) a coagulating agent, and wherein the salt is present in an amount to provide the composition with metallic or metalloid element content of at least 1 weight percent based on total weight of the composition.

10 2. The composition of Claim 1 wherein the hydrophilic polymer is a polyether polyol.

3. The composition of Claim 2 wherein the polyether polyol is a poly(oxyalkylene-oxyethylene) polyol.

15 4. The composition of Claim 3 wherein the poly(oxyalkylene-oxyethylene) polyol has an oxyethylene content of at least 35 weight percent based on total weight of the polyol.

5. The composition of Claim 3 wherein the oxyethylene of the polyol is distributed randomly throughout the polyol.

6. The composition of Claim 1 wherein the salt is present in an amount to provide a metallic or metalloid element content of at least 5 weight percent.

20 7. The composition of Claim 1 wherein the metallic or metalloid element is one or more substances selected from the Periodic Table of Elements as listed in Group 2a to 6a, Group 1b to 8, lanthanides and actinides.

25 8. The composition of Claim 1 wherein the metallic or metalloid element comprises lanthanum, barium, strontium, chromium, zirconium, yttrium, aluminum, lithium, iron, antimony, bismuth, lead, calcium, magnesium, copper, boron, cadmium, cesium, cerium, dysprosium, erbium, europium, gold, hafnium, holmium, lutetium, mercury, molybdenum, niobium, osmium, palladium, platinum, praseodymium, rhenium, rhodium, rubidium, ruthenium, samarium, scandium, sodium, tantalum, thorium, thulium, tin, zinc, nickel, titanium, tungsten, uranium, vanadium, ytterbium, or combinations of two or more of 30 thereof.

9. The composition of Claim 1 wherein the coagulating agent is an organic or inorganic substance having an aqueous pH value greater than 7.

10. The composition of Claim 9 wherein the coagulating agent is an organic substance which comprises a primary or secondary, amine, amide or alkanolamine.

5 11. The composition of Claim 9 wherein the coagulating agent is an inorganic base.

12. The composition of Claim 11 wherein the inorganic base is ammonium hydroxide.

13. The composition of Claim 1 wherein the coagulating agent is an 10 organic or inorganic substance having an aqueous pH value of less than 7.

14. The composition of Claim 13 wherein the coagulating agent is an inorganic substance.

15. The composition of Claim 14 wherein the coagulating agent is 16 hydrogen sulfide.

16. The composition of Claim 1 wherein the hydrophilic organic polymer is a poly(oxyalkylene-oxyethylene) polyol that has a randomly distributed oxyethylene content of at least 35 weight percent based on total weight of the polyol; and wherein the coagulating agent is an alkanolamine.

17. The composition of Claim 1 wherein the hydrophilic organic 20 polymer is a poly(oxyalkylene-oxyethylene) polyol that has a randomly distributed oxyethylene content of at least 35 weight percent based on total weight of the polyol; and wherein the coagulating agent is ammonium hydroxide.

18. A process for preparing a metal-based powder having a mean 25 particle size of less than 1 micrometer by calcining at a temperature of from 300°C to 3000°C a composition that comprises:

a) liquid hydrophilic organic polymer; and

b) an aqueous salt solution containing at least one metallic or metalloid element;

30 characterized in that the composition further comprises a coagulating agent, and the salt is present in an amount to provide the composition with metallic or

metalloid element content of at least 1 weight percent based on total weight of the composition.

19. The process of Claim 18 wherein the hydrophilic organic polymer is a poly(oxyalkylene-oxyethylene) polyol that has a randomly distributed oxyethylene content of at least 35 weight percent based on total weight of the polyol; and wherein the coagulating agent is an alkanolamine.

20. The process of Claim 19 wherein the hydrophilic organic polymer is a poly(oxyalkylene-oxyethylene) polyol that has randomly distributed oxyethylene content of at least 35 weight percent based on total weight of the polyol; and wherein the coagulating agent is ammonium hydroxide.

21. A method for solidifying a mixture which contains a liquid hydrophilic organic polymer with an aqueous salt solution of at least one metallic or metalloid element which comprises adding to said mixture a coagulating agent or precursor thereto.

22. The method of Claim 21 wherein the coagulating agent comprises ammonium hydroxide or an alkanolamine.

23. The method of Claim 21 wherein a precursor of the coagulating agent is urea.

24. The method of Claim 23 wherein thermal decomposition of the urea provides the *in situ* generation of the coagulating agent.

25. The method of Claim 22 wherein the polyether polyol is a poly(oxyalkylene-oxyethylene) polyol that has a randomly distributed oxyethylene content of at least 35 weight percent based on total weight of the polyol.

26. The method of Claim 22 wherein the aqueous metal salt solution is present in an amount to provide the mixture with a metal salt content of at least 10 weight percent based on total weight of the mixture.

INTERNATIONAL SEARCH REPORT

Int'l. Application No

PCT/US 98/12306

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6	B22F9/24	C01F1/00	C01G1/00	C04B35/622	C01B13/18
	C01B21/06	C01B31/30	C01B17/20		

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B22F C01F C01G C04B C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 929 433 A (HEXEMER JR RICHARD L ET AL) 29 May 1990 see column 4, line 1 - line 47 see example IV see claims ---	1,7-9, 11,12, 18,21
X	EP 0 395 243 A (ICI PLC) 31 October 1990 see whole document ---	1,7-9, 18,21
A	US 5 188 780 A (LANGE FREDERICK F ET AL) 23 February 1993 see whole document ---	1-26

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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PCT/US 98/12306

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